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(54) **METHOD OF MANUFACTURING SEMICONDUCTOR DEVICES INCLUDING GENERATING AND ANNEALING RADIATION-INDUCED CRYSTAL DEFECTS**

(71) Applicant: **Infineon Technologies AG**, Neubiberg (DE)

(72) Inventors: **Johannes Georg Laven**, Taufkirchen (DE); **Hans-Joachim Schulze**, Taufkirchen (DE); **Moriz Jelinek**, Vienna (AT); **Werner Schustereder**, Villach (AT)

(73) Assignee: **Infineon Technologies AG**, Neubiberg (DE)

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(58) **Field of Classification Search**

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USPC ..... 438/107, 198, 308, 369, 378, 474, 475, 438/491, 499, 502, 506, 508, 509, 510, 513, 438/535, 544, 663; 257/E21.006, E21.043, 257/E21.051, E21.054, E21.077, E21.115, 257/E21.125, E21.126, E21.127, E21.134, 257/E21.135, E21.147, E21.248, E21.319, 257/E21.321, E21.32, E21.347

See application file for complete search history.

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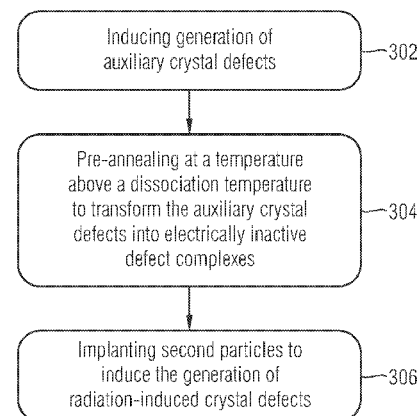
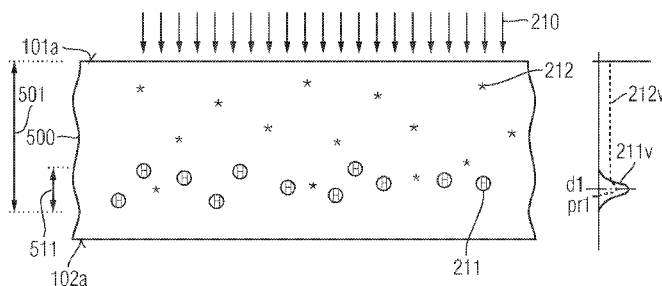
Primary Examiner — David Nhu

(74) Attorney, Agent, or Firm — Murphy, Bilak & Homiller, PLLC

(57) **ABSTRACT**

The generation of auxiliary crystal defects is induced in a semiconductor substrate. Then the semiconductor substrate is pre-annealed at a temperature above a dissociation temperature at which the auxiliary crystal defects transform into defect complexes, which may be electrically inactive. Then protons may be implanted into the semiconductor substrate to induce the generation of radiation-induced main crystal defects. The defect complexes may enhance the efficiency of the formation of particle-related dopants based on the radiation-induced main crystal defects.

**16 Claims, 5 Drawing Sheets**



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FIG 1A

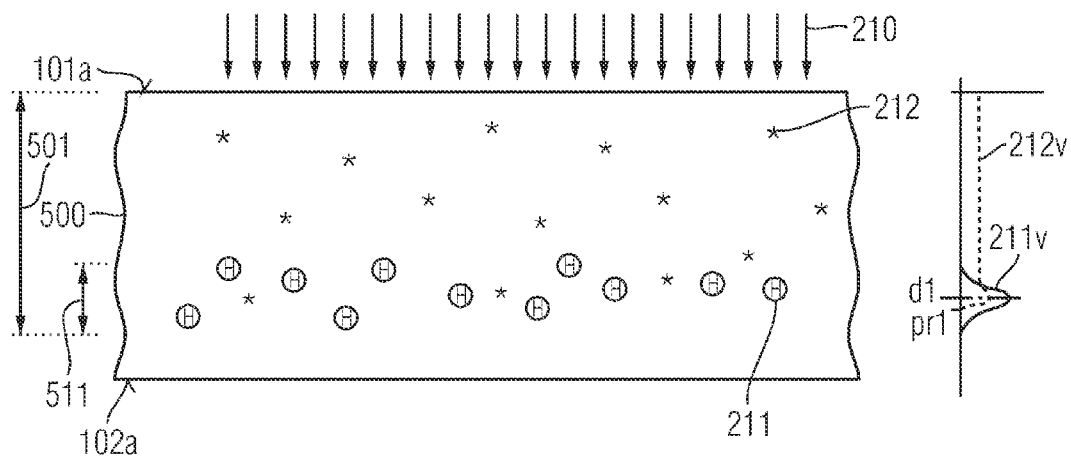


FIG 1B

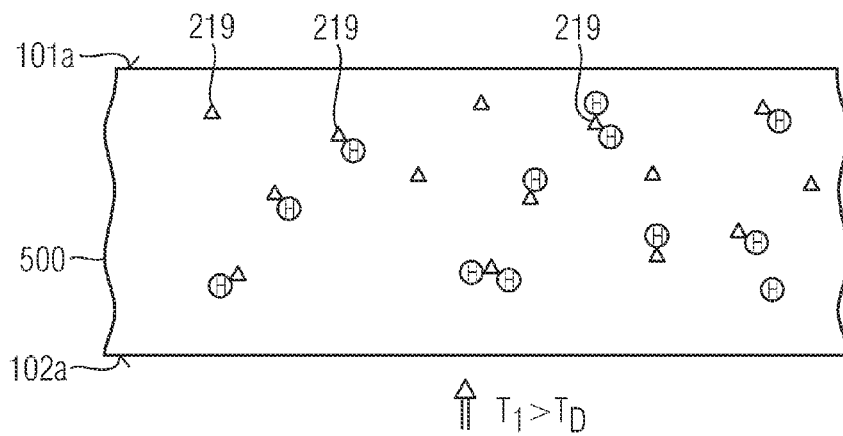


Diagram of a thin film 500. The film is bounded by surfaces 101a (top) and 102a (bottom). It contains various particles: triangles (some with a plus sign), stars, and circles (some with a plus sign, some with a star). A specific particle is labeled 219. A dashed line indicates a profile 229v. A vertical axis on the right is labeled N (up) and d (down). A temperature condition  $T_2 < T_D$  is indicated by two upward arrows at the bottom.

FIG 2A

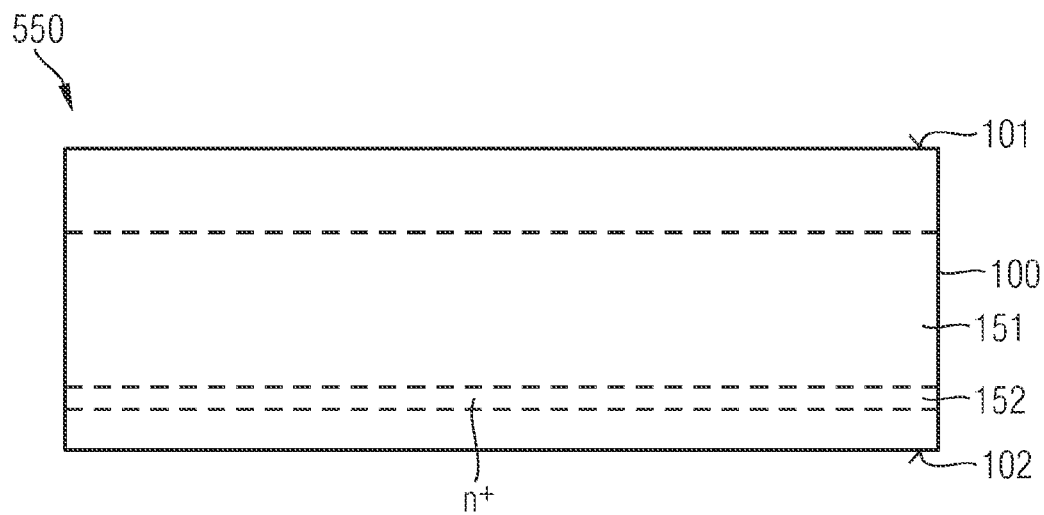


FIG 2B

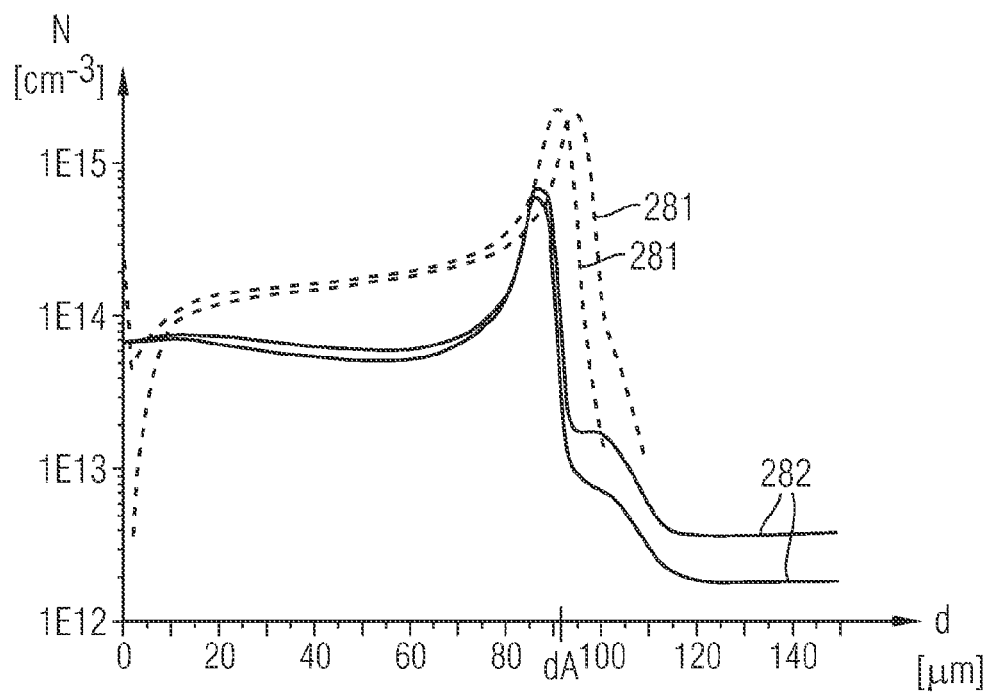


FIG 3A

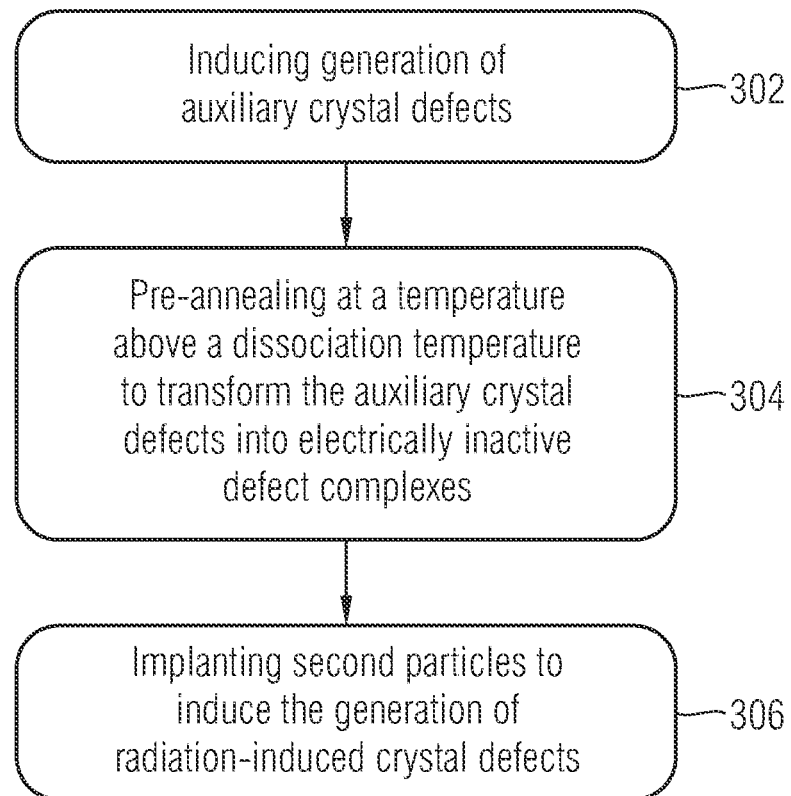
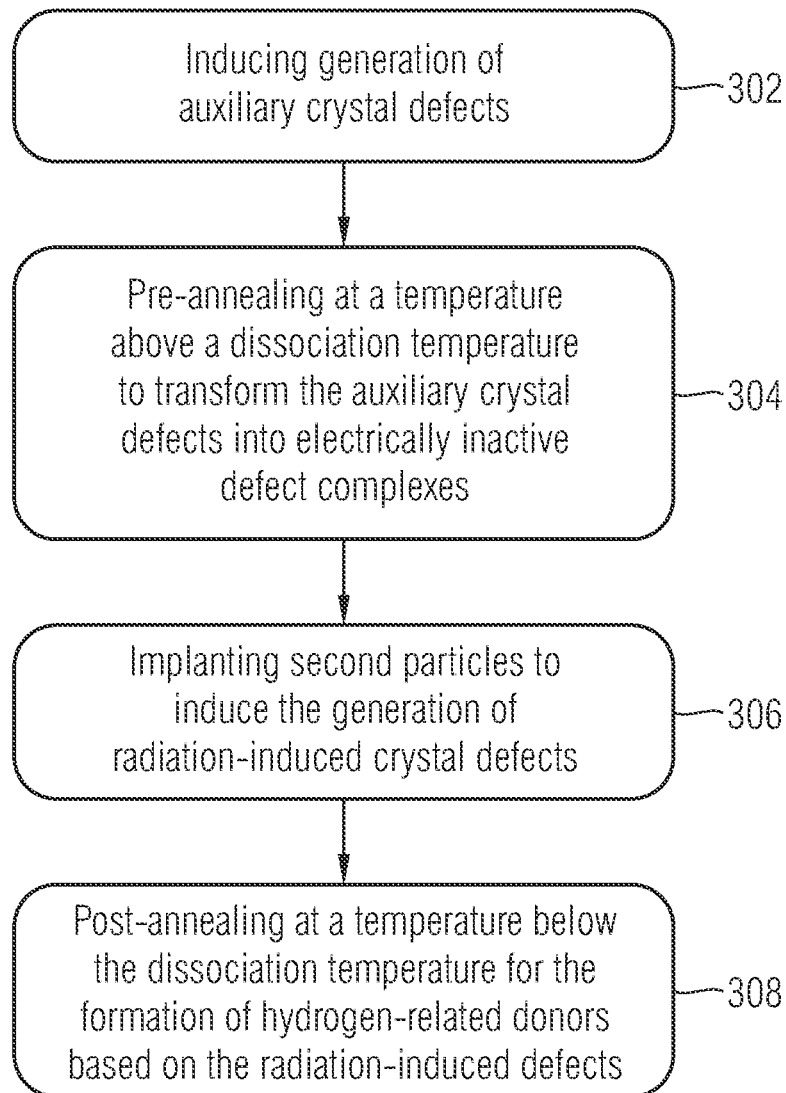


FIG 3B



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# METHOD OF MANUFACTURING SEMICONDUCTOR DEVICES INCLUDING GENERATING AND ANNEALING RADIATION-INDUCED CRYSTAL DEFECTS

## BACKGROUND

Particle beams irradiated on a single-crystalline semiconductor substrate generate radiation-induced crystal defects. Radiation-induced crystal defects decorated with non-doping impurity atoms such as hydrogen and/or oxygen may be effective as doping centers. For example, annealing a silicon crystal after a proton implant at temperatures between 270 and 470° C. may form stationary and stable hydrogen-related donors. It is desirable to expand the range of possible applications for radiation-induced doping centers and to improve the efficiency of methods for forming doped regions using particle beams containing non-doping atoms.

## SUMMARY

According to an embodiment a method of manufacturing a semiconductor device includes inducing generation of auxiliary crystal defects in a semiconductor substrate. Then the semiconductor substrate is pre-annealed at a temperature above a dissociation temperature at which the auxiliary crystal defects transform into defect complexes. Then main implant particles are implanted into the semiconductor substrate, wherein implanting the main implant particles induces the generation of radiation-induced main crystal defects.

According to another embodiment a semiconductor device includes a semiconductor body with parallel first and second surfaces. The semiconductor body contains hydrogen-related donors. A concentration profile of the hydrogen-related donors vertical to the first surface includes a maximum value of at least  $1 \times 10^{15} \text{ cm}^{-3}$  at a first distance to the first surface and does not fall below  $1 \times 10^{14} \text{ cm}^{-3}$  over at least 60% of an interval between the first surface and the first distance.

Those skilled in the art will recognize additional features and advantages upon reading the following detailed description and on viewing the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification. The drawings illustrate the embodiments of the present invention and together with the description serve to explain principles of the invention. Other embodiments of the invention and intended advantages will be readily appreciated as they become better understood by reference to the following detailed description.

FIG. 1A is a schematic cross-sectional view of a portion of a semiconductor substrate for illustrating a method of manufacturing a semiconductor device according to an embodiment, after implanting auxiliary implant particles.

FIG. 1B is a schematic cross-sectional view of the semiconductor substrate portion of FIG. 1A after pre-annealing the semiconductor substrate.

FIG. 1C is a schematic cross-sectional view of the semiconductor substrate portion of FIG. 1B after implanting main implant particles.

FIG. 1D is a schematic cross-sectional view of the semiconductor substrate portion of FIG. 1C after post-annealing.

FIG. 2A is a schematic cross-sectional view of a portion of a semiconductor device with an implant layer including particle-related dopants according to a further embodiment.

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FIG. 2B is a schematic diagram illustrating a vertical concentration profile of the particle-related dopants in the semiconductor device of FIG. 2A.

FIG. 3A is a simplified flowchart for illustrating a method of manufacturing a semiconductor device according to a further embodiment.

FIG. 3B is a simplified flowchart for illustrating another method of manufacturing a semiconductor device according to a further embodiment including a post-anneal.

## DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings, which form a part hereof and in which are shown by way of illustrations specific embodiments in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural or logical changes may be made without departing from the scope of the present invention. For example, features illustrated or described for one embodiment can be used on or in conjunction with other embodiments to yield yet a further embodiment. It is intended that the present invention includes such modifications and variations. The examples are described using specific language, which should not be construed as limiting the scope of the appending claims. The drawings are not scaled and are for illustrative purposes only. For clarity, the same elements have been designated by corresponding references in the different drawings if not stated otherwise.

FIGS. 1A to 1D illustrate the formation of particle-related dopants in a semiconductor substrate **500**, wherein generation of the particle-related dopants includes inducing generation of main crystal defects by implanting main implant particles **211** in a main implant process.

The semiconductor substrate **500** may be a semiconductor wafer, for example a silicon wafer, an SOI (silicon-on-insulator) wafer, e.g. an SOG (silicon-on-glass) wafer or a substrate of another single-crystalline semiconductor material such as silicon carbide SiC, gallium arsenide GaS, gallium nitride GaN or another  $A_{III}B_V$  semiconductor, germanium Ge or a silicon germanium crystal SiGe. According to an embodiment the semiconductor substrate **500** is a silicon wafer obtained by a Czochralski process, for example an m:Cz (magnetic Czochralski) silicon wafer with an oxygen content from  $1 \times 10^{17} \text{ cm}^{-3}$ , for example at least  $2 \times 10^{17} \text{ cm}^{-3}$ , to  $4 \times 10^{17} \text{ cm}^{-3}$ .

The semiconductor substrate **500** may have a first surface **101a** and a second surface **102a** parallel to the first surface **101a**. In the following a normal to the first surface **101a** defines a vertical direction and directions parallel to the first surface **101a** are lateral directions. The semiconductor substrate **500** may include non-doping impurity atoms such as interstitial oxygen atoms.

In the semiconductor substrate **500** the generation of auxiliary crystal defects is induced, e.g., by surface processes generating excess crystal vacancies. For example, the semiconductor substrate **500** may be subjected to a rapid thermal anneal in a nitrogen containing atmosphere at a temperature greater than 1000° C. and at a cooling rate greater than 20° C./min in the temperature range between the maximum temperature and 800° C. and a cooling rate greater than 5° C./min in the temperature range between 800° C. and 500° C.

According to the embodiment illustrated in FIG. 1A, the auxiliary crystal defects are radiation-induced defects induced by an auxiliary implant process. A first implant beam **210** containing auxiliary implant particles **211** such as electrons, neutrons, protons or light ions, for example helium



ions, incidents on the first surface **101a**. According to an embodiment the implant beam **210** contains protons at an acceleration energy of at least 2 MeV, for example at least 4 MeV and at an implant dose in a range from  $5\text{E}13$  to  $1\text{E}15\text{ cm}^{-2}$ , or  $1\text{E}14$  to  $5\text{E}14\text{ cm}^{-2}$ , e.g., about  $4\text{E}14\text{ cm}^{-2}$ . The auxiliary implant particles **211** traverse a first traversed layer **501** of the semiconductor substrate **500** between the first surface **101a** and a first particle range **pr1** and induce the formation of the radiation-induced auxiliary crystal defects **212** in the first traversed layer **501**.

After the auxiliary implant process, the semiconductor substrate **500** contains the auxiliary crystal defects **212** in the traversed layer **501** as well as the auxiliary implant particles **211** in the first implant layer **511**. The vertical concentration profile **212v** of the auxiliary crystal defects **212** is approximately constant in a portion of the first traversed layer **501** between the first surface **101a** and the first implant layer **511**, may have a shallow peak within the first implant layer **511** and may decline from the shallow peak within the second particle range **pr1**. The vertical concentration profile **211v** of the auxiliary implant particles **211** is approximately a Gaussian distribution with the maximum value at a first implant distance **d1** determined by the acceleration energy of the auxiliary implant particles **211**.

Proceeding to FIG. 1B, the semiconductor substrate **500** is pre-annealed at a first anneal temperature **T1** greater than a dissociation temperature **TD** of the auxiliary crystal defects **212**. The auxiliary crystal defects **212** may include core complexes which after dissociation of the auxiliary crystal defects **212** may transform, e.g., agglomerate to high-order crystal defect complexes **219** containing vacancies and oxygen **VnOm**, thereby optionally incorporating to some degree hydrogen atoms contained in the semiconductor substrate **500**. The crystal defect complexes **219** may be electrically inactive, i.e., they are not effective as donors or acceptors. The hydrogen atoms may stabilize the defect complexes. For silicon substrates the first anneal temperature **T1** is at least  $500^\circ\text{C}$ ., for example at least  $510^\circ\text{C}$ . or at least  $550^\circ\text{C}$ .

The hydrogen atoms may be intrinsic impurities or may be introduced by the previous proton implant. In case the first implant beam **210** does not contain protons, hydrogen atoms may be introduced into the semiconductor substrate, e.g. by in-diffusion from a hydrogen plasma source before, during or after the auxiliary implant process.

FIG. 1B shows crystal defect complexes **219** that may be electrically inactive and that may getter hydrogen atoms present in the semiconductor substrate **500**. The crystal defect complexes **219** may provide more getter places than occupied by previously implanted protons. The concentration of free hydrogen atoms is lower than before the pre-anneal and may be lower than before the first implant process. The pre-anneal may convert at least a portion of the auxiliary crystal defects **212** of FIG. 1A or approximately all of them into crystal defect complexes **219**. The pre-anneal may last at least one hour or at least three hours, for example at least five hours and increases the efficiency of a following doping process.

In the main implant process illustrated in FIG. 1C, a second implant beam **220** irradiates the first surface **101a** of the semiconductor substrate **500**. The second implant beam **220** includes main implant protons **221**. A second implant distance **d2** may correspond to the first implant distance **d1** of the first implant beam **210** in FIG. 1A, or may be smaller than the first implant distance **d1**.

According to other embodiments a vertical impurity concentration profile **221v** of the implanted main implant protons **221** has a maximum at a second implant distance **d2** which may be greater or smaller than the first implant distance **d1** in

FIG. 1A. In a second traversed layer **502** traversed by the implanted main implant protons **221** the main implant protons **221** induce the generation of radiation-induced main crystal defects **222**. Further implants at different implant energies and/or implant doses may follow.

FIG. 1C shows the main implant protons **221** concentrated in a second implant layer **512**, the radiation-induced main crystal defects **222** in a second traversed layer **502** between the first surface **101a** and a second particle range **pr2** as well as the crystal defect complexes **219** optionally stabilized by hydrogen atoms that may be introduced during the first implant process.

A post-anneal at a second anneal temperature **T2** below the dissociation temperature **TD** forms particle-related dopants **229** localized at the stationary and stable radiation-induced and vacancy-related main crystal defects **222** as shown in FIG. 1D.

The particle-related dopants **229** may be hydrogen-related donors of various species, e.g. hydrogen-related double donors (HDDs), shallow hydrogen-related donors (SHDs), or the like. For silicon substrates the second anneal temperature is between  $300^\circ\text{C}$ . and  $510^\circ\text{C}$ ., for example between  $400^\circ\text{C}$ . and  $500^\circ\text{C}$ . According to an embodiment the second anneal temperature is between  $470^\circ\text{C}$ . and  $495^\circ\text{C}$ . and the anneal lasts at least three, e.g. at least five hours.

The hydrogen-related donors **229** are formed predominantly in a zone around a second implant distance **d2**, where the concentration of the implanted main implant protons has a maximum. In the second implant layer **512** the concentration of the main implant protons is higher than the concentration of the second radiation-induced vacancy-related main crystal defects **222**. The formation of particle-related dopants **229** in the second implant zone **512** is mainly given by the number of radiation-induced vacancy-related main crystal defects **222**. In case of a proton implant, more hydrogen atoms are available in the second implant layer **512** than hydrogen atoms can be consumed for the formation of hydrogen-related donors.

A high concentration of surplus free hydrogen in the semiconductor substrate **500** may promote the formation of electrically inactive crystal defect complexes at the expense of the efficiency of formation of the hydrogen-related donors **229** such that the surplus hydrogen countervails the formation of hydrogen-related donors. For example, surplus hydrogen may promote the transformation of hydrogen-related donors into additional electrically inactive defect complexes or may induce another process competing with the formation of hydrogen-related donors.

Instead, the preconditioning including generation of auxiliary crystal defects and tempering them above the dissociation temperature **TD** generates crystal defect complexes **219** that getter some of the free hydrogen atoms and reduce the surplus hydrogen content or even form additional vacancy-hydrogen-related complexes acting as donors.

Hence the presence of the crystal defect complexes **219** increases the efficiency of the formation of hydrogen-related donors during the post-anneal. As a result, a lower overall implantation dose is sufficient for forming an n-type layer containing non-doping atoms. In addition, higher concentrations of particle-related dopants may be achieved than without the preconditioning.

The defect complexes **219** may also getter free oxygen atoms present in the semiconductor substrate **500**. For example, m:Cz silicon wafers (magnetic Czochralski silicon wafer) contain to some degree free interstitial oxygen atoms. During manufacturing of semiconductor devices from the semiconductor substrate **500** the free oxygen atoms may form

long chain thermal oxygen-related donors at a certain generation rate. The crystal defect complexes **219** may getter to some degree the interstitial oxygen atoms. The gettering of oxygen atoms at the defect complexes **219** competes with the formation of oxygen-related donors and hence reduces the formation of oxygen-related donors. As a result a higher concentration of interstitial oxygen can be tolerated in a virgin semiconductor substrate, e.g., in an m:Cz silicon wafer. For example, the above-described preconditioning may be applied to silicon substrates with an oxygen concentration of at least  $1\text{E}16\text{ cm}^{-3}$ , e.g., at least  $1\text{E}17\text{ cm}^{-3}$  or at least  $2\text{E}17\text{ cm}^{-3}$ .

After the auxiliary implant and before or after the pre-anneal or the post-anneal the semiconductor substrate **500** may be thinned from the second surface **102** up to an auxiliary plane at a target distance **td** to the first surface **101** in order to shape the vertical dopant profile of the finalized device. The target distance **td** may correspond to the first particle range **pr1** of FIG. 1A, the second particle range **pr2**, the first implant distance **d1** of FIG. 1A, or the second implant distance **d2** or may be smaller than the second implant distance **d2** such that the second implant layer **512** is largely or completely removed. According to another embodiment, the target distance **td** is selected such that a region of high dopant concentration may be formed close to or directly adjoining the final rear side surface obtained by the thinning process.

FIGS. 2A and 2B refer to a semiconductor body **100** of a semiconductor device **550**. The semiconductor device **550** may be a semiconductor diode or a semiconductor switching device, for example an IGFET (insulated gate field effect transistor) an IGBT (insulated gate bipolar transistor) or a thyristor. The semiconductor body **100** is based on a single crystalline semiconductor material, for example silicon Si, germanium Ge, silicon germanium SiGe, silicon carbide SiC, gallium arsenide GaS, gallium nitride GaN, another  $A_{III}B_{IV}$  compound semiconductor, germanium Ge or a silicon germanium crystal SiGe.

The semiconductor body **100** may have a first surface **101** which may be planar or which may include coplanar surface sections as well as a second surface **102** parallel to the first surface **101**. The semiconductor body **100** includes an implant layer **152** containing hydrogen-related donors, wherein an implant dose of a proton implant for generating the hydrogen-related donors is greater than  $1\text{E}14\text{ cm}^{-2}$ , e.g., greater  $4\text{E}14\text{ cm}^{-2}$ . Along a vertical direction perpendicular to the first surface **101** the concentration of the hydrogen-related donors steadily decreases between a maximum value within the implant layer **152** and both the first surface **101** and the second surface **102**.

According to an embodiment, the maximum value of the concentration profile of the hydrogen-related donors is at least  $1\text{E}15\text{ cm}^{-3}$ , e.g., at least  $3\text{E}15\text{ cm}^{-3}$  or  $1\text{E}16\text{ cm}^{-3}$ .

A further implant layer **151** may directly adjoin the implant layer **152**, wherein the concentration of hydrogen-related donors in the implant layer **152** is at least four times, e.g., at least ten times, as high as in the further implant layer **151**. A vertical extension of the further implant layer **151** may be at least twice as large as the vertical extension of the implant layer **152**. In the implant layers **151**, **152** the hydrogen-related donors may add to a uniform or stepped background doping of donors such as phosphorus P or arsenic As atoms.

The implant layers **151**, **152** may form combinations of a drift zone and a field stop layer, a barrier layer, recombination or injection zones, or portions thereof, by way of example.

FIG. 2B shows first concentration profiles **281** resulting from a process using the above-described preconditioning as well as second concentration profiles **282** for hydrogen-re-

lated donors formed according to comparative examples without preconditioning for high implant doses of at least  $2\text{E}14\text{ cm}^{-2}$ .

Conventionally, after a proton implant, the high hydrogen impurity concentration in and around the implant layer **152** locally countervails the formation of hydrogen-related donors. As a consequence, in a conventional implant layer **152** a maximum value of the concentration of the hydrogen-related donors does not exceed  $1\text{E}15\text{ cm}^{-2}$ . Further due to the higher hydrogen excess, in and close to the implant layer **152** the formation of the hydrogen-related donors is less effective than at a greater distance to the implant layer **152**. Hence, at high implant doses of at least  $2\text{E}14\text{ cm}^{-2}$ , the second concentration profiles **282** show minima between the implant surface and the concentration maximum. For the embodiment illustrated in FIG. 2B, the minima are in the range of  $60\text{ }\mu\text{m}$  to  $70\text{ }\mu\text{m}$ , i.e., close to the doping maximum around the end-of-range of the proton implantation. By contrast, since the preconditioning locally decreases the excess of hydrogen such that the countervailing effect of surplus hydrogen is partly accommodated, the first concentration profiles **281** resulting from the above-described preconditioning according to the embodiments show no local minima even at high implant doses of at least  $2\text{E}14\text{ cm}^{-2}$  or at least  $4\text{E}14\text{ cm}^{-2}$ .

Instead, for a maximum value of the hydrogen-related donor concentration of at least  $1\text{E}15\text{ cm}^{-3}$ , e.g., at least  $3\text{E}15\text{ cm}^{-3}$ , or, according to a further embodiment,  $1\text{E}16\text{ cm}^{-3}$ , at a first distance **dA** to the first surface **101**, the hydrogen-related donor concentration does not fall below  $1\text{E}14\text{ cm}^{-3}$  over at least 60%, e.g. at least 75%, of an interval between the first surface **101** and the first distance **dA**, wherein the first distance **dA** may be greater than  $40\text{ }\mu\text{m}$ , for example greater than  $60\text{ }\mu\text{m}$ . The first concentration profiles **281** may steadily decrease over at least 60% of the interval between the first surface **101** and the first distance **dA** with increasing distance to the first distance **dA**.

According to an embodiment, the first concentration profiles **281** may include one or more further local maxima between the first surface **101** and the first distance **dA**, wherein the local maxima have values lower than the maximum value at the first distance **dA**. According to another embodiment the first concentration profiles **281** steadily decrease from the maximum value at the first distance **dA** with decreasing distance to the first surface **101**. In addition the first concentration profiles **281** may steadily decrease from the maximum value at the first distance **dA** with decreasing distance to the second surface **102**.

FIG. 3A refers to a method of manufacturing a semiconductor device. The generation of auxiliary crystal defects is induced in a semiconductor substrate (**302**). The semiconductor substrate is pre-annealed at a temperature above a dissociation temperature at which the auxiliary crystal defects are transformed into electrically inactive crystal defect complexes (**304**). Main implant particles are implanted into the semiconductor substrate to induce the generation of radiation-induced main crystal defects (**306**). A post-anneal may induce the generation of particle-related donors based on the main crystal defects and the pre-annealed auxiliary crystal defects.

The method of FIG. 3B is similar to the method of FIG. 3A and further includes a post-anneal at a temperature below the dissociation temperature for the formation of hydrogen-related donors based on the radiation-induced main crystal defects (**308**).

Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that a variety of alternate and/or equivalent

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implementations may be substituted for the specific embodiments shown and described without departing from the scope of the present invention. This application is intended to cover any adaptations or variations of the specific embodiments discussed herein. Therefore, it is intended that this invention be limited only by the claims and the equivalents thereof.

What is claimed is:

1. A method of manufacturing a semiconductor device, the method comprising:
  - inducing generation of auxiliary crystal defects in a semiconductor substrate; then
  - pre-annealing the semiconductor substrate at a temperature above a dissociation temperature at which the auxiliary crystal defects transform into crystal defect complexes; and then
  - implanting main implant protons into the semiconductor substrate, wherein implanting the main implant protons induces a generation of radiation-induced main crystal defects.
2. The method of claim 1, wherein
  - the pre-annealing transforms the auxiliary crystal defects into electrically inactive crystal defect complexes.
3. The method of claim 1, further comprising:
  - post-annealing, after implanting the main implant protons, the semiconductor substrate at a temperature below the dissociation temperature to form particle-related dopants at the radiation-induced main crystal defects and the pre-annealed auxiliary defects.
4. The method of claim 1, wherein
  - inducing generation of the auxiliary crystal defects comprises implanting auxiliary implant particles.
5. The method of claim 4, wherein
  - the auxiliary implant particles are selected from a group consisting of protons, helium ions, neutrons and electrons.
6. The method of claim 4, further comprising:
  - removing at least a portion of the semiconductor substrate between an end-of-range peak of the main implant par-

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ticles and a surface opposite to a surface through which the auxiliary implant particles are implanted.

7. The method of claim 1, wherein
  - inducing generation of the auxiliary crystal defects comprises a rapid thermal anneal.
8. The method of claim 1, wherein
  - the semiconductor substrate includes a silicon crystal and the particle-related dopants are hydrogen-related donors.
9. The method of claim 1, wherein
  - the semiconductor substrate includes a silicon crystal and the pre-annealing is performed at a temperature greater than 500° C.
10. The method of claim 3, wherein
  - the semiconductor substrate includes a silicon crystal and the post-annealing is performed at a temperature between 270° C. and 500° C.
11. The method of claim 1, wherein
  - an implant dose of the main implant particles is greater than  $1 \times 10^{14} \text{ cm}^{-2}$ .
12. The method of claim 1, wherein
  - an implant dose of the main implant particles is greater than  $4 \times 10^{14} \text{ cm}^{-2}$ .
13. The method of claim 1, wherein
  - the auxiliary implant particles are protons.
14. The method of claim 1, wherein
  - implanting the auxiliary implant particles includes at least two different implant processes at different implant energies.
15. The method of claim 1, wherein
  - the semiconductor substrate is a magnetic Czochralski wafer containing interstitial oxygen at a concentration of at least  $1 \times 10^{17} \text{ cm}^{-3}$ .
16. The method of claim 1, further comprising:
  - diffusing hydrogen into the semiconductor substrate before the post-annealing.

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